

METHOD OF DEGASING MOLTEN STEEL**SPECIFICATION****FIELD OF THE INVENTION**

The present invention relates to a method of degassing
5 molten steel under vacuum whereby the degasification process is
accelerated by the addition of solids to the molten steel.

BACKGROUND OF THE INVENTION

The degassing of molten steel under vacuum in order to
increase the quality of the steel may utilize the addition of
10 solids to accelerate the degassing process. The latter depends
upon certain thermodynamic and kinetic principles and various
degassing mechanisms have been proposed.

The degassing process thermodynamically is a function
of the pressure dependency of the metallurgical reactions upon
15 chemical elements dissolved in the molten steel at an atomic
basis.

For the elements hydrogen and nitrogen, the following
relationships apply:



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$$(2) \quad [H] = k_H * (P_{\{H\}})^{\frac{1}{2}} \quad \text{and} \quad [N] = k_N * (P_{\{N\}})^{\frac{1}{2}}$$

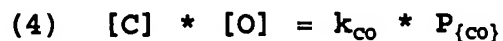
In these relationships $[H]$ represents the concentration of hydrogen and $[N]$ the concentration of nitrogen. In relationship {2} k_H and k_N are constants and the pressures are the partial pressures of hydrogen and nitrogen, respectively.

5 The concentrations of atomically dissolved elements, in the case of diatomic molecules is the proportional fourth root of the partial pressure in the surrounding gas phase (Sievert's law).

10 In the case of the element oxygen, its removal is largely a consequence with reaction of oxygen with carbon dissolved in the steel according to the relationship:



15 where $[C]$ is a concentration of carbon, $[O]$ is the concentration of oxygen and $\{CO\}$ is the concentration of carbon monoxide. In this reaction the gaseous reaction product carbon monoxide is formed. This process results in a simultaneous and combined reduction of the contents of both elements.



20 Here the product of the oxygen and carbon concentrations is directly proportional to the carbon monoxid

partial pressure in the surrounding gas phase. k_{co} is a constant.

By reducing the partial pressure in the gas phase with continuous evacuation of the process gases in the vacuum vessel, a reduction of the respective element level in molten steel can be obtained. With a sufficient treatment time, this will lead to a pressure-dependent equilibrium content of the chemical elements.

The process involves all of the steel phase/gas phase interfaces. As a result not only does the reaction proceed at the surface of the molten steel bath but also at the interfaces between the molten steel and gas formed by all bubbles of the gases within the melt since they form locations of reduced partial pressures of the respective elements. This applies especially for all vacuum processes for the treatment of molten steel in which inert gases are introduced into the melt. At these locations the inert gas has a dual function. On the one hand inert gas brings about a thorough mixing of the melt by convective transport while on the other hand the gas bubbles provide reduced partial pressure locations within the steel for dissolved gases and thus directly promote their removal.

In conjunction with the degasification kinetics, a basic precondition for the degasification process is the

transition of the elements from a dissolved state into the gaseous state. The transition from a gas dissolved in molten metal into the gas phase is comprised of a number of steps which taken together determine the speed of the degasification process.

5 These steps are:

a) Convective transport from the interior of the melt to a region close to the surface of the melt. From there to the gas phase above the melt there is a further transport to the interface by diffusion.

10 b) The transfer of the gas atoms from solution into and adsorbed at the metal surface.

c) The reaction of the gas atoms in the adsorbed layer either with one another to form diatomic molecules or with other atoms as for example in the formation of carbon monoxide.

15 d) Desorption of gas molecules from the surface of the melt.

e) Diffusion of the gas molecules in the ambient gas space apart from the transfer of gas molecules into the gas space at already existing interfaces (such as the bath surface of inert gas bubbles), in which the spontaneous formations of gas bubbles plays an important role.

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This degassing process presumes the existence of bubble-growth-promoting nuclei (bubble nuclei). For this equilibrium, the pressure in the interior of the bubble nuclei must be at least as high as the sum of the ambient pressure above the melt, the ferrostatic pressure of the melt column above the bubble nuclei and the capillary pressure which results from surface tension. The formation of gas bubbles within the melt takes place in different ways and can be considered a homogeneous bubble formation or a nonhomogeneous bubble nucleus formation.

The homogeneous formation of a stable hydrogen bubble nucleus, can occur only above an equilibrium pressure of 10^4 atm. Corresponding gas contents do not arise in steel-making processes. Homogeneous nuclei formation in the case of elemental hydrogen and nitrogen is therefore improbable and does not play any role in the processes with which the invention is concerned.

The heterogeneous formation of growth promoting bubble nuclei is facilitated on solid boundary layers. This is especially the case for porous, rough and crack-containing surfaces since there the contact angle of the bubble nucleus is small ($< 180^\circ$) and the interior pressure of a growing bubble can be less than the equilibrium pressure in the surrounding melt.

It is known that for these reasons formation of gas bubbles within a steel melt will develop on the surface of the

refractory lining as well as on solid slag particles. The gas bubbles which arise during the degasification by heterogeneous nuclei formation provide additional stirring in the melt and thus convective transport processes are accelerated. This in turn promotes degasification so that an autocatalytic and self-accelerating process can result.

The above-mentioned characteristics and relationships have been used for decades in practice for the removal of chemical elements like hydrogen, nitrogen and oxygen dissolved in molten steel.

Apart from these considerations which arise in practice, mention should be made of publications which are relevant. For example Okada et al describes for the RH process, i.e. the vacuum circulation process, also known as the Rheinstahl-Heraeus process, the acceleration of the decarbonization reaction below a bath carbon content of 20 ppm by blowing pulverulent iron oxide (Fe_2O_3) by means of a top lance into the melt. The iron oxide particles which are blown into the melt serve on the one hand as nuclei for the formation of CO bubbles and on the other hand as oxygen carriers for the decarbonization processes. Ladle pressures (1-2 Torr, 1.3-2.6 mbar) and lance spacings from the upper surface of the melt (3 m) must be so selected that a sufficiently deep penetration of the pulverulent material into the melt is ensured. The particle sizes of the

Fe_2O_3 powder pass a mesh width corresponding to sieve size 100 or 0.149 mm. Fe_2O_3 powder is fed for decarbonization at a rate of 20-60 kg/min.

Kikuchi et al (daily report of the proceedings of the
5 Sixth International Iron and Steel Congress, 1990, Nagoya, Japan
"Development of the Deoxidation Technique for Clean Steel
Production by the Pressure Elevating and Reducing Method", pages
527 ff.) describe the NK-PERM (Pressure Elevating and Reducing
Method) process which is a variant of the ladle degasing
10 technique which utilizes the heterogeneous nuclei formation of
nitrogen and solid nonmetallic inclusions for the removal thereof
and in this manner can improve the degree of oxidic purification.
For this purpose the melt is initially treated with nitrogen by
bottom flushing. In a connected vacuum treatment the dissolved
15 nitrogen is separated at the inclusions and is flushed therefrom.

U.S. Patent 6,235,084 B1 describes an aluminothermal
heating process during the RH treatment. The decarbonization is
carried out under vacuum in a first stage in which oxygen is
blown in and then a composite metallic substance like, for
20 example, aluminum powder is introduced. The solid reaction
product Al_2O_3 which is thereby dispersed in the melt can serve as
the nuclei former for CO bubbles in the subsequent
decarbonization stage. As a result the decarbonization speed is
increased and the decarbonization duration is reduced.

As stated previously, the degasification reactions are pressure-dependent reactions. They encompass the removal of gases dissolved in molten steel like, for example, hydrogen and nitrogen and, when degasification is referred to here, it also includes the reduction of dissolved oxygen in molten steel which can be brought about by formation of carbon monoxide. The reactions are determined by the pressure relationships including the pressure above the steel surface of the melt and factors like the mixing rate and the steel circulation rate as well as factors relevant to the apparatus used.

Conventional processes have various problems associated with them. One of them is the ability of the suction pump or pumps to obtain sufficiently low working pressures. In many cases the suction capacity must be very high and hence the capital costs for evacuation must also be high.

Another problem is the consumption of the medium required to obtain the requisite steel circulation. When a gas lift pump system is provided, the medium volume may be very high. Gas lift may be effected with argon or nitrogen. Earlier systems also have very long vacuum treatment times and this contributes to a high degree of wear of the refractory lining for the metallurgical vessels used.

OBJECTS OF THE INVENTION

It is the principal object of the present invention to provide an improved process for accelerating the degasification process for molten steel.

Another object of the invention is to provide an improvement in the utilization of the apparatus for degasifying molten steel by increasing productivity and reducing the vacuum treatment time and thereby increasing the useful life of the metallurgical vessels.

It is another object of the invention to improve the quality of the steel produced by a degasification process, namely, by reducing the final content of dissolved gases in the molten steel.

SUMMARY OF THE INVENTION

These objects and others which will become apparent hereinafter are attained in accordance with the invention which is a method of accelerating the degasification of molten steel under vacuum which comprises introducing solids promoting the degasification process, not in a pulverulent form, but rather as pieces of a size from 2 to 50 mm and not at some time after the commencement of degasification but directly upon the commencement of the degasification and especially within the first 5 minutes of degasification.

The fact that the solid pieces introduced into the melt are in the form of a fine granulate and are continuously charged into the melt for heterogeneous bubble nuclei formation, has been found to be critical to the improvement of the invention.

5 The introduction of the solid (by application to the surface of the melt), by blowing it into the melt and/or by blowing it onto the melt at the inception of and during the vacuum treatment ensures the heterogeneous bubble nuclei formation which accelerates degasing reaction.

10 The size and specific gravity of the granulate, i.e. a grain size of 0.2 to 50 mm and a preferred specific gravity which is sufficient to cause it to penetrate into the melt ensures a relatively deep penetration without special expenditure for apparatus like blowing lances at a short distance from the bath
15 and thus a high tendency to distortion.

 By comparison with earlier systems in which fine powder is introduced into the melt, the material losses by the application of suction to the vacuum vessel are largely avoided. As compared with the blowing of a powder onto the melt, the
20 efficiency of the suction treatment is increased. Furthermore, there is a significant reduction in contamination or loading of the vacuum generating unit.

The solid pieces, according to the invention, are introduced with the inception of degasification, namely during the starting phase and especially in the first five minutes. This has been found to improve the acceleration of the degasification and particularly the decarbonization process.

Depending upon the physical characteristics of the material, the process can be operated at a higher pressure level, i.e. above a pressure of 2 mbar. A pressure above 2 mbar appears to promote the formation of carbon monoxide.

The pieces of solid degasification promoter can be added at a rate of 20 to 100 kg/min. The upper pressure limit can be 150 mbar.

Since the introduction of powder by a lance is eliminated, the preferred introduction of the solids is via a metering device, for example a distributor trough or a cell wheel gate from a vacuum bunker or bin.

Because of the acceleration of the degasing process, the degasing duration can be shortened for a given final content of the gases in the steel. As a consequence the productivity of the apparatus can be increased and this contributes to an increase in the specific life of the refractory lining of the

vessel in RH apparatuses and the steel ladle. The result is a reduction in operating cost.

For the same treatment time as with conventional technology, a lower final content of the dissolved gases can be obtained. As a consequence a direct improvement of the technological properties of the steel is obtainable. In the case of the decarbonization process, a carbon level can be achieved which allows carbon containing and inexpensive additives like FeMn, i.e. FeMn of high purity, can be avoided in this case.

BRIEF DESCRIPTION OF THE DRAWING

The above and other objects, features, and advantages will become more readily apparent from the following description, reference being made to the accompanying drawing in which:

FIGS. 1 and 2 are graphs which illustrate the example described below; and

FIG. 3 is a cross section through an RH apparatus for carrying out the invention.

SPECIFIC DESCRIPTION

FIG. 3 shows an apparatus 10 for carrying out the invention which comprises a lined vessel 11 with a refractory lining 12 for a bath 13 of molten steel covered by a slag layer 14.

The treatment vessel 15 has dip tubes 16, 17 extending into the melt, the tube 16 being a riser (arrow A) and the tube 17 being a descender (arrow B) so that the molten steel circulates through the vessel 15 convectively and, if desired, promoted by a pumping system such as a gas lift.

The vacuum is applied to the vessel 15 at 18 by the usual suction pumps. A vacuum bunker 19 containing 5 to 50 mm pieces of the additive, e.g. scrap metal, ore (especially iron ore), slag or FeMn, or mixtures thereof, has a vibrating trough 20 for metering these pieces 21 into the molten metal in the vessel 15.

Specific Example

This example involves the treatment of ULC melts (ultralow carbon melts) in accordance with the invention.

The tests were made on a 265 metric ton RH apparatus to investigate the acceleration of the decarbonization process with ultralow carbon products at the lowest carbon levels. The pieces introduced into the melt at the starting phase of the decarbonization were pieces of iron or which were continuously added by a vibrating trough from a vacuum bunker at a pressure in the treatment vessel greater than 2 mbar but not exceeding 5 mbar. The feed rate was 40 kg/min. The size of the positions of the iron ore were between 3 and 10 mm. The melt was sampled

after 10 and 15 minutes and had an original carbon content of 200 to 250 ppm.

FIGS. 1 and 2 show the results of the tests in terms of the ratio of the cumulative frequency in percent to the carbon content in ppm with and without iron ore addition after a
5 decarbonization time of 10 minutes (FIG. 1) and of 15 minutes (FIG. 2).

After the same decarbonization duration, the melt with iron ore addition have a significantly lower carbon content. The
10 carbon contents measured after 10 minutes of decarbonization show that the decarbonization velocity especially at the early stages of the decarbonization are accelerated, the iron ore addition being effected in this early stage.

The invention thus accelerates or promotes the
15 degasification processes or the chemical reactions with gaseous reaction products in the secondary metallurgical treatments of the molten raw steel under vacuum. The productivity of the apparatus is increased, the steel quality is improved and the production cost reduced.

20 The vacuum treating apparatuses which can be used for the process of the invention include ladle stand degasifiers, ladle degasifiers and degasifiers which treat only part of a

batch at a time, for example, the RH circulating melt degasifiers, DH (vacuum lift) apparatus, also known as Dortmund-Hörder process units, vacuum degasing or VD units generally and REDA (Revolutionary Degasing Accelerator) units.

5 Other methods of introducing the solids may also be used. For example an immersion lance as in the VD apparatuses, RH and REDA units with a hockey stick below the suction nozzle, REDA, RH and VD units with vacuum bunkers or gates with or without distributor troughs, RH units with blowing of the solids
10 in through tuyeres, and REDA, RH and VD units which blow the solids onto the surface of the melt with lances.